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CITATION:

Kiyama, Masao ...[et al]. The Formation and Growth of a-FeO Particles by Transformation of γ-FeO in Alkaline Media. Bulletin of the Institute for Chemical Research, Kyoto University 1988, 65(5-6): 187-191

ISSUE DATE:

1988-03-15

URL:

http://hdl.handle.net/2433/77211

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 65, No. 5-6, 1987

The Formation and Growth of α-Fe_2O_3 Particles by Transformation of γ-Fe_2O_3 in Alkaline Media

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Received September 10, 1987

The fine Fe_3O_4 particles with the mean particle size, D, 20 nm were subjected to autoclaving at temperatures between 120 and 280°C in aqueous solutions of either H_2O_2 or $NaNO_3$. In the presence of $NaNO_3$ the Fe_3O_4 particles were chemically stable at 200°C or below, whereas they were oxidized to γ-Fe_2O_3 particles in the presence of H_2O_2. Some particles of them transformed into platelike α-Fe_2O_3 ones at temperatures higher than 200°C, the α-Fe_2O_3 content in the products depending on the kind of an oxidant, and the reaction temperature and time. The transformation of γ-Fe_2O_3 into α-Fe_2O_3 in aqueous solutions was accelerated in the presences of H_2O_2 and NaOH, whereas it was hinderded in alkaline solutions containing Si(IV). An increase in the NaOH concentration promoted the growth for the (001) surfaces(basal planes) of α-Fe_2O_3 particles. As the D of γ-Fe_2O_3 particles was increased, the growth for the (001) surfaces of α-Fe_2O_3 particles by autoclaving at 250°C was hindered.

KEY WORDS: Autoclaving/ Transformation/ Platelike Particle/ Fe_3O_4/ γ-Fe_2O_3/ α-Fe_2O_3

I. INTRODUCTION

It is well known that fine particles of Fe_3O_4 are easily oxidized in air to γ-Fe_3O_4 without changes in particle size and shape.[1] When the precipitates, prepared by a wet method, consists of extremely fine particles of Fe_3O_4 the aggregation of particles is caused by heat-treatment in air during the course of drying. The fine Fe_3O_4 particles in an acidic suspension were gradually oxidized to γ-Fe_2O_3 with air and transformed with the changes in particle size and shape into α-Fe_2O_3 even at such a low temperature as 70°C.[2] On the other hand, the Fe_3O_4 particles in an alkaline suspension were very stable under oxidizing conditions at atomspheric pressure.

In this paper, the conditions for the oxidation of Fe_3O_4 to extremely fine particles of γ-Fe_2O_3, and for transformation into α-Fe_2O_3, both in aqueous solutions with pH≥7 by autoclaving at below 280°C, will be reported together with the shape and size of the resulting α-Fe_2O_3 particles.

Experimental

Chemicals of an analytical grade were used except sodium silicate. Water glass containing 30 wt% Na_2SiO_3 used was chemical guaranteed grade. Water was deionized and distilled before use.

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Some precipitates of Fe_3O_4 were prepared by the same procedure as previously described.[3] Briefly the black precipitates, consisting of cubic Fe_3O_4 particles with greater than 50 nm in size, were prepared by air oxidation at 70°C of alkaline suspensions of $Fe(OH)_2$, their mean particle sizes being controlled by varying the concentrations of excess NaOH and Fe (II) in the starting suspensions. The black precipitate A, consisting of extremely fine particles, was prepared by air oxidation at 70°C of an aqueous suspension containing 0.2 M(1 M=1 mol/dm^3) Fe (II), 0.11 M Fe (III), and 1.0 M excess NaOH.

The black precipitates thus obtained were well washed with water until the chloride test gave a negative result, and separated from the solution by filtration. Except for the black precipitate A, they were treated with acetone, dried in air and subjected to heat-treatment in air at 200°C for 10 h to form the brownish, ferromagnetic powders (γ-Fe_2O_3).

The filtered precipitate A, containing 50 wt% Fe_3O_4, was stored in a polyethylene container. A part was taken from the precipitate and dried under reduced pressure to give the powdery sample for physical investigations.

Each sample(corresponding to 6.2–6.4 mmol iron ions; 0.5 g as a powder) was dispersed by an ultrasonic stirring into 50 mL(1 mL=1 cm^3) in a cylindrical tetrafluoethylene bottle(70 mL). The bottle containing the suspension was stoppered with a tetrafluoethylene cap, immersed in water contained in the 300 mL autoclave made of stainless steel to prevent the reduction of the volume of the suspention during the course of autoclaving, and heated to a desired temperature ranging from 120 to 280°C at the rate of 4°C/min. The suspension was kept at this temperature without stirring for different times and then allowed to cool to room temperature. The resulting products were well washed with water, filtered and then dried at 110°C in air.

The samples were examined by X-ray powder diffraction using FeKα radiation and transmission or scanning electron microscope(TEM or SEM). The Fe_3O_4 and γ-Fe_2O_3 samples were subjected to the BET surface area measurement using nitrogen and their mean particle sizes, D, were estimated from the BET surface area by assuming that the sample consisted of cubic particles of 5.2 (Fe_3O_4) or 5.0 (γ-Fe_2O_3) specific gravity. The average particle size, d, for the sample A was further estimated from the line broadening of X-ray diffraction peak for the (311) plane of spinel structure. The α-Fe_2O_3 content in a mixture of α-Fe_2O_3 and γ-Fe_2O_3 obtained by autoclaving was estimated from the relative intensities of the X-ray diffraction peak for d(104) α-Fe_2O_3 and d (400) γ-Fe_2O_3.

RESULTS and DISCUSSION

Oxidation of Fe_3O_4 *particles in aqueous solutions.* The black precipitate A in the muddy form, whose D and d values were 20 and 30 nm respectively, was resuspended into water in the bottle and to this suspension either $NaNO_3$ or H_2O_2(each 6 mmol) as an oxidant was added. The suspensions were subjected to autoclaving at 120, 150, 200, 250 and 280°C for 20 and 40 h. The black precipitate A was found to be chemically stable in the presence of $NaNO_3$ at temperatures between 120 and 200°C, whereas it was oxidized to a brown precipitate (γ-Fe_2O_3) in the presence of H_2O_2 at 150°C without the changes in particle shape and size. Some particles in the black precipitate were transformed into platelike particles of α-Fe_2O_3 at above 200°C, regardless of the kind of oxidant, the α-Fe_2O_3 content in the products depending on the kind of oxidant and the reaction temperature and time.

The transformation into α-Fe_2O_3. A brown precipitate A as the starting material was prepared in the presence of 18 mmol H_2O_2(=0.36 M) from the suspention(50 mL) of the black precipitate A (5 g in a muddy form) by autoclaving at 150°C for 40h. The Mössbauer absorption spectrum taken at room temperature showed that the brown precipitate A consisted of the spinel phase and contained no Fe (II) ions at the B sites in the spinel structure. It was filtered and also stored as a muddy form containing 50 wt% Fe_2O_3.

The brown precipitates A were resuspended into water and NaOH solutions of 0.1 and 4.0 M. Each suspension was subjected to autoclaving at 250°C for 5 h. The presence of 0.1 M NaOH caused to promote the transformation into α-Fe_2O_3 from 30 to 90% in the α-Fe_2O_3 content by autoclaving, the α-Fe_2O_3 content being independent of the NaOH concentration. When similar experiments were carried out with the alkaline suspensions containing 0.1 M NaOH and either 6 or 30 mmol H_2O_2, the brown precipitates A were completely transformed into the nonferromagnetic precipitates by autoclaving at 250°C.

According to our other experiments, it was difficult to oxidize all the Fe (II) in the Fe_3O_4 particles with keeping its crystal structure. The brown precipitate A probably contained a slight amount of Fe (II) which could not be detected by the physical examination. Such a slight amount of the Fe (II) remaining in some particles in the precipitate might hinder the transformation by autoclaving. Consequently the presence of H_2O_2 in the starting alkaline suspension was indispensable for the oxidation of the Fe (II). SEM photographs of two typical α-Fe_2O_3 samples are given in Fig. 1, together with TEM of the brown precipitate A. An increase in the NaOH concentration to 4M accelerates the growth for the (001) surfaces(basal plane) of platelike α-Fe_2O_3 particles by autoclaving at 250°C. In the X-ray diffraction pattern of α-Fe_2O_3 particles, the intensity of the (110) peak relative to the (104) peak varied with the sample. This was because the platelike particles in the pressed powdery sample for X-ray analysis underwent alignment to some extent. The degree of alignment depended on the aspect rations of the particles and on the packing density.

The alkaline suspentions containing 0.2 M NaOH, 0.18 M(9 mmol) H_2O_2 and one of 0.05 M triethanolamine, sodium oleate, stearate, dodecyl benzen sulfonate or silicate were also subjected to autoclaving at 250°C for 5 h. No remarkable difference was found in the transformation and particle growth by autoclaving except for the presence of sodium silicate. The presence of Si (IV) was found to hinder the transformation.

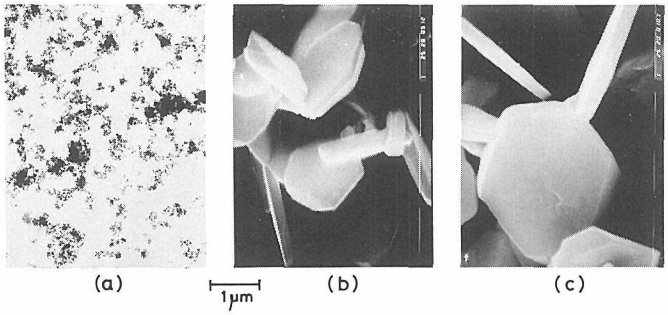

Fig. 1. SEM photographs of α-Fe_2O_3 particles obtained by autoclaving at 250°C suspensions of γ-Fe_2O_3 particles (TEM(a)) in the presences 0.12 M H_2O_2 and either 0.1 (b) or 4.0 M NaOH (c).

In order to study of the Si(IV) concentration on the transformation, the alkaline suspensions containing 0.1 M NaOH, 0.12 M H_2O_2 and different amounts of Si (IV) 1–20 wt% of Fe_2O_3 present (corresponding to 3.6-72 mM Si (IV)) were subjected to autoclaving at 250°C for 5 h. The α-Fe_2O_3 content in the products decreased with increasing the Si (IV) concentration and reached 0% with 18–72 mM Si (IV). TEM photographs of three typical samples are given in Fig. 2.

The brown precipitate treated in the presence of 72 mM Si (IV) separated from the solution by filtration (not washed with water) was heat-treated in air at 500, 600, 700 and 800°C for 4 h. The transformation into α-Fe_2O_3 began to proceed at 700°C and was completed

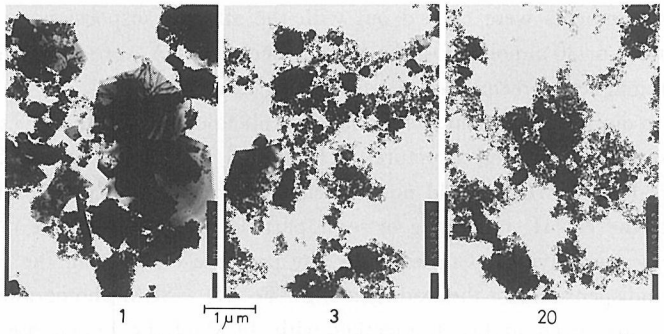

Fig. 2. TEM photographs of samples obtained by autoclaving at 250°C γ-Fe_2O_3 particles in the presences of 0.12 M H_2O_2, 0.1 M NaOH and different amounts of Si (IV). Number below each photo. indicates the amount of Si (IV) in wt%.

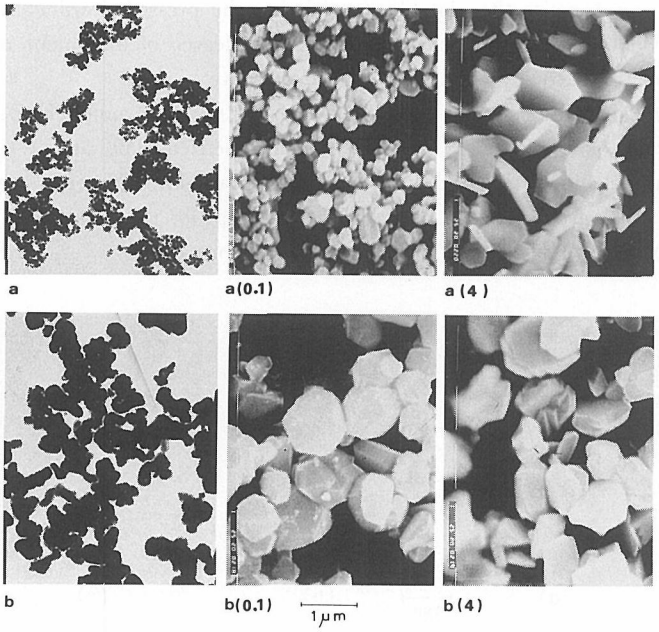

Fig. 3. SEM photographs of transformation products(α-Fe_2O_3) from γ-Fe_2O_3 particles with 0.06 (a) and with 0.25 μm in D (b). Number in parentheses indicates the NaOH concentration in M.

at 800°C with a slight increase in particle size. The γ-Fe_2O_3 precipitate A containing no Si (IV) was transformed into α-Fe_2O_3 with an increase in particle size at 600°C. The temperature for the transformation became higher with hinderance of sintering between the γ-Fe_2O_3 particles coated by the Si (IV) layers as has been known.[4)]

Some of γ-Fe_2O_3 particles in the alkaline suspension containing less than 18 mM Si (IV) are considered to be incompletely coated with the Si (IV) and to transform into α-Fe_2O_3 by autoclaving at 250°C or by heat treatment at 600°C or above.

In order to investigate the effect of the particle size of the γ-Fe_2O_3 samples on the transformation at 250°C and the particle growth, the powdery γ-Fe_2O_3 samples with D=60, 130 and 250 nm were used in place of the brown precipitate A. The suspensions containing 0.9 M H_2O_2, and either 0.1 or 4.0 M NaOH were subjected to autoclaving at 250°C for 5 h. The γ-Fe_2O_3 particles were all transformed, irrespective of the D values and concentration. SEM photographs of typical transformation products are shown in Fig. 3, together with TEM photographs of the original γ-Fe_2O_3 samples. The experimental results demonstrate that an increase in the D values of the γ-Fe_2O_3 sample hinders the growth of the (001) surfaces of α-Fe_2O_3 particles with the transformation.

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